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TGA (inert as LOI), TGA-MS and TGA-FTIR Methods as Analytical Tools to Measure Residual Moisture on Pure and Impure Plutonium and Uranium Oxides

Executive Summary

Thermal gravimetric (or thermo-gravimetric) analysis (TGA) in an inert (argon or helium) test chamber (TGA-inert) provides a conservative estimate of the residual moisture in actinide-bearing materials and associated impurities. A TGA coupled with a Fourier Transform Infrared (FTIR) detection system or a mass spectrometry (MS) detection system directly measures residual moisture on materials. The TGA-MS and TGA-FTIR methods can be applied to any material to show that it meets the residual moisture standard in DOE-STD-3013-2000.

This paper documents the material types that have been adequately tested using the TGA-inert, TGA-MS and TGA-FTIR methods. Testing and analysis was performed at LANL, Hanford's Plutonium Process Support Laboratories, and the Rocky Flats analytical laboratory.

Introduction

A TGA instrument coupled with a FTIR detection system or a MS detection system can directly measure residual moisture (Randall Erickson, April 2002). These analytical methods were approved by EM-1 in May 2002 (Jessie Roberson, 2002). DOE sites are required to identify materials that can be measured using these methods and to provide the technical basis. TGA with an inert test chamber (TGA-inert or TGA-inert as LOI) measures residual moisture on actinide-bearing materials with associated impurities when the total weight change from room temperature to 1000°C is used (Randall Erickson, April 2002). TGA-inert, TGA-MS and TGA-FTIR analysis methods can be applied to any material represented by items in the MIS inventory to show that the material meets the residual moisture requirement of DOE-STD-3013-2000. The TGA residual moisture measurement methods developed are now approved for 3013-stabilized oxides to complement the already approved LOI method. Thermal gravimetric analysis, as traditionally used, is an instrument and technique that measures residual moisture or any other volatile mass loss and is an equivalent method to the standard LOI method. Mass loss is the underlying principle of both methods. TGA is used with an inert (non-oxidizing) test chamber atmosphere to analyze any material that may oxidize during the analysis because the oxidation of a material may result in a weight gain. This gain may, in turn, mask the weight loss resulting from residual moisture loss during the heating cycle. All three methods (TGA-inert, TGA-MS, and TGA-FTIR) are performed in an inert environment of argon or helium. Argon is preferred over helium because it more efficiently purges air from the TGA test chamber.

The TGA Working Group (TGA-WG) has demonstrated that the TGA-MS and TGA-FTIR are acceptable methods for analyzing a stabilized material's residual moisture content and that a material meets the residual moisture standard in DOE-STD-3013-2000. This work is supported by the Los Alamos National Laboratory 94-1 R&D team and the Materials Identification and

Surveillance Working Group (MIS-WG). Additionally, the TGA-inert method can analyze stabilized materials for compliance with the residual moisture standard in DOE-STD-3013-2000. TGA working group is comprised of engineers and scientists at the DOE facilities at Los Alamos National Laboratory (LANL), Rocky Flats (RFETS), Richland Laboratories (Hanford), and Savannah River Site (SRS) with additional help of the instrument manufacturer, Netzsch Gerategau GmbH. The technical basis reports are LA-UR-02-2233 (Morales, et al., 2002), LA-UR-02-3728 (Morales, Gallegos and Barney, 2002), letter M2E00-PPSL-02-007 (Barney, June 2002), LA-UR-02-0310 (Morales et al., January 2002), LA-UR-02-5625 (Jachimowski and Paffett) and LA-UR 02-2946 (Jachimowski and Paffett).

In this context, a conservative measurement reports at least as much or more residual moisture in the sample than is actually present. For example, the TGA analysis demonstrates that U_3O_8 experiences oxygen loss above 800°C (a weight decrease) and it is known that that NaCl and KCl evaporate above 800°C. In the TGA-inert analysis method, all such weight loss is counted as residual moisture. While these results are undesirable, they are conservative with respect to actual moisture content and are acceptable in that they only result in unneeded restabilization, rather than allowing a potentially unsafe condition in the storage container. The TGA-inert method results in more conservative measurements than the other two methods. For some materials, TGA-inert may be so conservative that unacceptable reworking rates result.

This report notes the materials that have been validated for use on the TGA (inert as LOI), TGA-MS and TGA-FTIR moisture measurement methods. Testing on plutonium-bearing materials has been performed, primarily at LANL and Hanford's Plutonium Process Support Laboratories, to support the use of TGA-inert, TGA-MS, and TGA-FTIR for residual moisture measurements.

Application of the Methods to Measure Actinide Materials with Associated Impurities

These three measurement methods can be used on feed streams of pure plutonium oxides and impure oxides containing major impurities of uranium, sodium and potassium salts; magnesium oxides and chlorides; calcium oxides and salts; and magnesium hydroxides that are present in MIS items (see Table 1), and in the materials described in Hanford letter M2E00-PPSL-02-007. These measurements are performed after the materials are stabilized in accordance with conditions specified in DOE-STD-3013-2000.

TGA-inert

The TGA-inert or TGA (inert as LOI) method is approved for measuring residual moisture on materials as noted above. It is used on materials that are stabilized according to the conditions specified in DOE-STD-3013-2000. This method does not provide a direct residual moisture measurement, but, rather, a conservative moisture estimate.

TGA-MS

The TGA-MS method approved for measuring the moisture on plutonium-bearing materials as noted above (Roberson, May 14, 2002 and Erickson, 19 April 19 2002). There are no restrictions, on the materials that can be analyzed using this method. However, development of and strict compliance to maintenance and quality control procedures is required. Since the measurement

method is dependent on the transfer of residual moisture from the TGA crucible through the TGA chamber and through tubing to the mass spectrometer, the temperature at all points must be sufficiently high to ensure that the residual moisture released reaches the detector. In addition, volatiles such as NaCl and KCl may condense at orifices, bends in the transfer lines, and on other equipment surfaces, thus plugging or restricting gas flow to the detector. Maintenance and routine measurements of known standards must be done frequently enough to ensure that the instrument is performing correctly.

TGA-FTIR

The TGA-FTIR method is approved for measuring the moisture on plutonium-bearing materials as noted above (Roberson, 14 May 2002 and Erickson, 19 April 2002). There are no restrictions on the materials that can be analyzed using this method. However, strict compliance to maintenance and quality control procedures is required during TGA-MS analysis. Some impurities may react with the IR detector window and change the detection parameters. Maintenance and routine measurements of known standards must be done frequently enough to ensure that the instrument is performing correctly.

Technical Basis

Application of these TGA methods to measure residual moisture in actinide materials is based on analysis method evaluations and analysis of materials at RFETS, SRS, Hanford, and Los Alamos. The technical basis for each of the methods is sufficiently robust to sanction their use on materials that are stabilized according to DOE-STD-3013-2000. LA-UR-02-3728 describes tests on MIS items with significant quantities of K, Na, and Ca salts. These materials are expected to be the most difficult to analyze with the MS and FTIR instruments because they contain impurities that volatilize at high temperatures (i.e., temperatures greater than 750°C), but are not carried to the detector or out of the system because they condense at temperatures lower than 750°C. Presuming the successful analysis of these materials is reported in LA-UR-02-3728, other materials in the MIS inventory should be easily analyzed using these TGA methods. Nevertheless, to ensure that a problem has not been overlooked and to develop a broader technical basis, additional MIS samples will be analyzed during 2002 and 2003 and the LA-UR-02-3728 report will be updated as the data is available. Sites using TGA-inert, TGA-FTIR, and TGA-MS will notify the MIS-WG of any anomalies discovered during 3013 stabilization and packaging. This information will be included in updates to this report as appropriate.

Table 1 lists MIS items, site identifiers, and originating processes. Materials listed in Table 1 were generally characterized using the analyses described in "Represented Items in the MIS Project," (Roberson, 2002). In addition to the MIS items listed in Table 1, Hanford materials CML-U/Pu Oxides, MgO-PuO₂ co-precipitation oxides, miscellaneous solution oxides, DPF oxides, and production DPF oxides were evaluated at Hanford (Barney, 2002). TGA tests on MISNE4 are equivalent to testing the individual items 520610020, 11589, C06032A, TS707013, 1000089, and 39-01153. Items 5501407, CAN92, PSU-84-06-05, SCP711-56, SCP711-46, contain uranium.

Table 1. Items in the MIS inventory

MIS SAMPLE ITEM	Site ID	CURRENT PROCESS [MIS]	Source Site	COMMENT / POINT OF ORIGIN
TS707001	061	Metal Oxidation	RFETS	Thermal Stabilization, Building 707 J-Module After 1995
11589	060	Metal Oxidation	RFETS	Thermal Stabilization, Building 707 J-Module Before 1990
11608	060	Metal Oxidation	RFETS	Thermal Stabilization, Building 707 J-Module Before 1990
7221730	061	Metal Oxidation	RFETS	Metal and Chip Burning, Building 771 Room 114
TS707013	061	Metal Oxidation	RFETS	Thermal Stabilization, Building 707 J-Module After 1995
5501579	061	Hydride Oxide	RFETS	Hydride Operations Building 779, Rooms 152A / 160A
1000089	080	Precipitation and Calcination of the Peroxide	RFETS	Precipitation - Calcination, Building 371, Room 3511
ARF-102-85-114-1	N/A	Assumed to be Precipitation and Calcination of Peroxide	HANFORD	WG Oxide received from Rocky Flats
7161856	081	Precipitation and Calcination of the Peroxide	RFETS	Calcination, Building 771, Room 114
PPSL-365	N/A	Direct de-nitration	HANFORD	Converted from nitrate in PFP PPSL calciner
PBO-47-09-012-023	N/A	Continuous Oxalate Precipitation/Calcination	HANFORD	Converted from purified nitrate/PUREX Ncell
BLO-39-11-14-004	N/A	Continuous Oxalate Precipitation/Calcination	HANFORD	Converted from purified nitrate/PFP RMA Line
ATL27960	C217	Precipitation and Calcination of the Oxalate	LANL	--
MT-1490	653	High Purity Plutonium Oxide Bearing Np	RFETS	Plutonium Metallurgy R&D, Building 771, Room 182
PSU-84-06-05	N/A	Recovery from Pyrolytic Processing	RFETS	Mixed Oxide recovered from polycube/PFP
SCP711-46	N/A	Hot Plate oxidation	LANL	Fuel Pellets and powder
SCP711-56	N/A	Hot Plate oxidation	LANL	Fuel Pellets and powder
39-01153	054	By-product Oxide from Hydroxide Precipitation	RFETS	Caustic Waste Treatment, Building 371, Room 1115
05501407	Y61	Hydride Oxide/ By-product Plutonium-Uranium Oxide	RFETS	Hydride Operations Building 779, Rooms 152A / 160A
ARF-102-85-355	N/A	Assumed to be Oxide from Residue Processing	HANFORD	WG Oxide received from Rocky Flats
62750	U61	By-product Plutonium-Uranium Oxide	RFETS	Dissolution, Building 371, Room 1115
669194	Y61	By-product Plutonium-Uranium Oxide	RFETS	Special Assembly Projects, Building 777
053038	Y61	By-product Plutonium-Uranium Oxide	RFETS	Hydroxide Precipitation, Building 771

MIS SAMPLE ITEM	Site ID	CURRENT PROCESS [MIS]	Source Site	COMMENT / POINT OF ORIGIN
CAN92	061	By-product Plutonium-Uranium Oxide	RFETS	Analytical Lab Production Support, Building 559
520610020	061	Oxide from Pyrochemical Processes	RFETS	Pyrochemistry Technology Development, Building 779
C00695	086	Oxide from Pyrochemical (ER tilt pour) Processes	RFETS	ER tilt pour operations, Building 371. Calcined and stored in the B371 S/R at one time
CLLANL025	067	Oxide from Pyrochemical (ER tilt pour) Processes	RFETS	ER tilt pour operations, Building 371
ARF-102-85-295	N/A	Assumed to be Scrap Oxide from Pyrochemical Process	HANFORD	WG Oxide received from Rocky Flats
ARF-102-85-365	N/A	Assumed to be Scrap Oxide from Pyrochemical Process	HANFORD	WG Oxide received from Rocky Flats
ARF-102-85-223	N/A	Assumed to be Scrap Oxide from Pyrochemical Process	HANFORD	WG Oxide received from Rocky Flats
C06032A	159	Screenings from Oxide packaged for off site shipment	RFETS	Split Can - Calcined then stored in the B371 S/R at one time
C0024	146	Oxide from Pyrochemical Processes? - IDC is LOI reject – unsure of source	RFETS	Calcined then stored in the B371 S/R at one time
7032282	062	Dissolution Residuals (from foundry and scrap oxide)	RFETS	Oxide Dissolution, Building 771, Room 114
7242201	289	Dissolution Residuals (from foundry and scrap oxide)	RFETS	Residue Dissolution, Building 771, Room 149, Line 24
7242165	289	Dissolution Residuals (from foundry and scrap oxide)	RFETS	Residue Dissolution, Building 771 Room 149, Line 24
R437	N/A	Mg(OH) ₂ Precipitation/Calcination	HANFORD	From Purified Nitrate
R440	N/A	Mg(OH) ₂ Precipitation/Calcination	HANFORD	From Impure Nitrate (Concentrated Filtrate)
7242141	159	Screenings from Oxide packaged for off site shipment	RFETS	Building 771, Line 24
MISNE2	N/A	Mix of 7221730, TS707001, 11608 and 62750	Rock Flats	Pure items combined, V-blended, gypsum added and calcined numerous times
MISNE4	N/A	Mix of 520610020, 11589, C06032A, TS707013, 1000089, and 39-01153	Rocky Flats	Impure Items (Mg and Ca) combined, V-blended, gypsum added and calcined numerous times
LOX-1, -2, -3, -4, -5, -6	C217/ C211	Metal Oxidation	LANL	LANL
LM's 55-62, 98-105	M011	metal	LANL	--
LM's 1-54, 63-97	M011	metal	LANL	--

LA-UR-02-3728 establishes the technical basis for using the TGA-inert, TGA-FTIR, and TGA-MS methods for analyzing impure oxides. The tests described in LA-UR-02-3728 show how residual moisture is measured in these impure oxides. Material from items MISNE4, ARF-102-85-295, C00695, CAN92 05501407, Hanford CML, and 053038 were tested. Item 053038 has high calcium and chlorine content; C00695 has high sodium content; ARF-102-85-295 has high Mg, K, Na, and Cl content; and MISNE4 has high Mg, Ca, Cl, and Na content. The TGA data on ARF-102-85-295 measured by Morales and reported in LA-UR-98-994 (Toupadakis, March 1998), show significant potassium and sodium salt volatilization above about 750°C. These materials were specifically chosen because they contain these salts. The analyses described in LA-UR-02-3728 show that the residual moisture is removed in the TGA instrument and measured by the MS and FTIR instruments. In the TGA-MS and TGA-FTIR analysis systems, these salts are expected to create the most adverse environment in the test chamber while measuring the residual moisture, thus constituting the highest challenge to residual moisture measurements accuracy and precision. Since these materials are the most difficult to analyze difficulties or analysis problems during the evaluation of other materials that are represented materials in the MIS inventory are not expected.

Letter M2E00-PPSL-02-007 (Barney, 29 June 2002), establishes the technical basis for using these methods on completely stabilized plutonium oxides precipitated by magnesium hydroxide or oxalic acid from several solution types. Solution sources and characteristics included pure product nitrate, critical mass lab with mixed U/Pu, single and double pass filtrates, and miscellaneous solutions containing high levels of metallic impurities. Although actual process double pass filtrate oxides analyzed using the TGA-MS or weight loss measurement did not comply with the residual moisture limits (i.e., the weight loss and residual moisture content were greater than 0.5 wt.%), all of the total residual moisture values based on measured weight loss are more conservative than the TGA-MS measurement. These analyses show TGA removes the residual moisture and the mass spectrometer measures it. The mass spectrometry analysis results obtained from the impure oxides produced at the PFP thus far show that no significant amounts of residual moisture are evolved above 600°C.

The TGA function in the TGA-MS and the TGA-FTIR analysis methods is the same as the TGA function in the TGA-inert technique. In all three measurement methods, the material is placed in a TGA crucible, the furnace purged with the inert gas, and the material heated to 1000°C in the inert environment. A non-conservative error could be generated if air was used in the TGA chamber or water reacted with substoichiometric oxide before it desorbed from the surface of the material on heating. The material could react with air to increase the weight of the sample, for example UO_2 oxidation to U_3O_8 . However, MIS items CAN92, 669194, SCP711-56, SCP711-46, and 5501407, and Hanford CML items contain uranium. Letter M2E00-PPSL-02-007 (Barney, 29 June 2002), report LA-UR-02-2233 (Morales, et al. 2002) and report LA-UR-02-3728 (Morales, Gallegos and Barney report, 2002) show that residual moisture is removed and the material does not oxidize when heated in an inert environment. The TGA data alone can be used by any of the methods as long as all of the weight loss is attributed to the loss of residual moisture from the material tested. Report LA-UR-02-2946 (Jachimowski and Paffett, 2002), a thermodynamic evaluation of moisture-actinide interactions, establishes further that TGA in an inert environment is a conservative method to analyze for residual moisture content.

The three methods under discussion in this report have not yet been approved for analyzing materials that were potentially sub-stoichiometric (ie. PuO_{y-x} , $x>0$). Consideration of reaction kinetics and thermodynamics in carbon-moisture-sub-stoichiometric actinide oxide systems has revealed that residual moisture desorbs from the surface of the actinide before significant reaction occurs. (Jachimowski and Paffett). The authors could foresee of no plausible mechanisms by which a false pass result will occur under designed operational processes. If carbon were present the reaction of water and carbon to produce CO and CO_2 would result in a mass loss from the sample that is greater than that of desorption of water. If carbon scavenges oxygen from metal oxides during the TGA measurement, CO or CO_2 will evolve and desorb, again overestimating the water content. Thus oxidation of carbon by water should, at best, produce a false failure moisture measurement and will not negatively bias the moisture test. Empirical measurements establishing the validity of this point would be very beneficial and should be given high priority in the near term 94-1 research and development activity tasking. Another general recommendation is that TGA methods are superior to the LOI technique because the atmosphere, heating rate and experimental protocol afford a much greater control over experimental variability.

Summary and Conclusions

TGA analysis, accompanied by MS and FITR analysis, of numerous MIS samples, surrogate materials, and Hanford materials demonstrates the ability of TGA-inert, TGA-MS and TGA-FTIR to measure moisture on the materials that are anticipated in the packaging campaigns. TGA-MS and TGA-FTIR measure the moisture evolved from MIS items, based on evaluations on pure, mixed, and impure oxides. Samples representing the Rocky Flats processes of metal oxidation, hydride oxidization, precipitation and calcination of the peroxide, by-product oxide from hydroxide precipitation, by-product plutonium-uranium oxide, oxide from pyro-chemical processes, dissolution residuals, and screenings from oxide were tested. Hanford solution sources including pure product nitrate, critical mass lab with mixed U/Pu oxides, single and double pass filtrates and miscellaneous solution oxides are also part of the technical basis database. Analysis of all of the impure oxides in the MIS inventory was not accomplished, but those that were tested were materials that are anticipated to be problematical. The analysis methods were shown to be effective on these materials.

Additional MIS samples will be analyzed during 2002 and 2003 and the evaluation report LA-UR-02-3728 will be updated, as the data is available, in order to expand the technical basis to use these analytical methods. Sites using TGA-inert, TGA-FTIR, and TGA-MS will notify the MIS WG if any anomalies are discovered during 3013 stabilization and packaging. This information will be included in updates to LA-UR-02-3728 as appropriate. The DOE-STD-3013-2000 standard requires that each DOE site have sufficient controls on residual moisture sampling and analysis procedures to assure that the residual moisture measurements of stabilized and packaged oxide are accurate or that the measurement is a conservative measurement.

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